

Appendix E Sample Manipulation Instructions

E.1 Filtration Techniques (Liquid Media)

E.1.1 Scope and application. This instruction outlines two different techniques for the filtration of aqueous media (i.e., ground water, surface water, and potable water). The procedures address in-line filtration, where the filter assembly is under positive pressure, and vacuum filtration, where the filter assembly is under negative pressure. In addition, the procedures describe and recommend specific filtration equipment. Filtration of aqueous samples is performed when the removal of silt algae, particulates, and other debris is desired. Predominantly, filtration is employed when water samples are to be tested for dissolved metals. However, many regulatory agencies no longer accept filtered samples as representative of “dissolved metals” concentrations. Therefore, the position of the regulators should be investigated to assure acceptance of the data generated from these types of samples. An alternative procedure to filtration may be the use of low-flow sampling techniques. Filtered samples for metals (dissolved fractions) should be analyzed in conjunction with nonfiltered samples to determine the metal concentration in solution versus metals associated with solids. Analysis of both filtered and unfiltered samples will allow the determination of metal concentration associated with the solid. Samples requiring organic analyses are not filtered unless specifically requested in the field sampling plan. Filtration techniques for ground water should be conducted in the field shortly after collection and before the addition of preservatives. A delay in the filtration of these samples may allow potential changes in carbon dioxide and oxygen concentrations, effectively changing the water pH and Eh, and leading to metals precipitation. These particulates are then erroneously filtered and may lead to a negative bias in the filtered sample results.

E.1.2 Filtration techniques. The following instructions will focus on in-line positive and negative pressure filtration of aqueous media. In-line filtration is recommended because it provides better consistency through less sample handling and minimizes sample exposure to the atmosphere. In the instructions, specific types of filtration devices will be referenced. For assessment of dissolved concentrations of major ions and trace metals, 0.1- μ m filters are recommended, although 0.45- μ m filters are normally used for most regulatory programs. In addition, analytical methods used to determine dissolved metal concentrations have historically used 0.45- μ m filters to separate dissolved and particulate phases. Therefore, if the filter pore size is changed, comparability between existing and newly generated data must be evaluated. Filters must be prerinsed following manufacturers’ instructions. When no recommendations for prerinsing exist, pass a minimum of 1 L of water through the filter prior to sampling. For ground water this is done after purging is complete and before the sample collection.

E.1.2.1 Positive pressure filtration. Positive pressure filtration methods are preferred for aqueous sample filtration. Aqueous samples that may require positive pressure filtration include ground water samples, surface water samples, and potable water supply samples. To filter an aqueous sample using the positive pressure technique, a pump, filter, and tubing are required. The following are examples of equipment that may be used for positive pressure in-line filtration.

E.1.2.1.1 Pump system.

- High-flow range: 3 - 2,300 mL/min
- Low-flow range: 6 - 460 mL/min
- System flow control: $\pm 10\%$

E.1.2.1.2 Filter assembly.

- Groundwater sampling capsule: 6 to 12 mm (1/4 to 1/2 in.), tapered barb fitting
- Pore size: 0.45 mm or as dictated by project
- Continuous use pressure: 413.6 kPa (60 psi) at ambient conditions
- Maximum momentary pressure: 689 kPa (100 psi) at ambient conditions

E.1.2.1.3 Filtration procedure.

- C Use polytetrafluoroethylene (PTFE) (PTFE is commonly referred to using the registered name of Teflon) tubing for pump and filter connections.
- C Connect the appropriately sized in-line filter to the discharge tubing from the pump. Make sure the flow arrow on the filter is pointing in the correct direction and the system is leakproof.
- C Apply pressure to the liquid sample (via pump) to force it through the filter directly into the appropriate sample container at a pressure recommended by the equipment manufacturer.
- C Replace the in-line filter when the flow becomes too restricted because of a buildup on the filter. To replace the filter, discontinue pumping (turn off pump), relieve the pressure in the system (line between the pump and the filter), and disconnect the filter and replace with a new one.
- Preserve the sample as necessary and verify that the pH is sufficient for the criteria.
- C Verify that a PTFE liner is present in the cap. Secure the cap tightly.
- Label the sample bottle with an appropriate label. Be sure to include all necessary information.
- Record the information in the field logbook and field sheet, and complete all chain-of-custody documents (see Instruction F-1, "Documentation," Appendix F).
- Release the pressure in the filtration equipment, disconnect sample filtration device from the discharge tubing, and thoroughly decontaminate or properly dispose of all equipment and materials in accordance with the project sampling and analysis plan.

E.1.2.2 Negative pressure filtration. Aqueous samples that may require negative pressure filtration include ground water samples, surface water samples, and potable water supply samples. To filter an aqueous sample using the negative pressure technique, a pump, filter, sample collection container, and tubing are required. The following equipment may be used for negative pressure (vacuum) filtration:

E.1.2.2.1 Pump system, hand-operated vacuum/pressure pump

- Maximum vacuum: 25 in. Hg
- Maximum pressure: 103.4 kPa (15 psi)
- Composition: metal or polyvinyl chloride (PVC)

E.1.2.2.2 Filter assembly, Nalgene filter funnel/collection flask

- Filter composition: cellulose nitrate
- Pore size: 0.45 μ m or as dictated by project
- Collection flask capacity: 500 mL (16.5 fl oz)
- Composition of assembly: Polystyrene (sterilized)

E.1.2.2.3 Filtration procedure.

- C Select a presterilized filter assembly with a filter of appropriate pore size.
- C Connect vacuum tubing to the pump and the filter assembly. Use PTFE tubing for pump and filter connections and verify that it is leakproof.
- C Pour the aqueous sample into the filter funnel portion of the filtration assembly. Avoid excessive turbulence or agitation of the sample, or transferring solids that may have settled to the bottom of the sample container.
- C Using a vacuum pump, create a negative pressure as recommended by the equipment manufacturer in the collection vessel of the filtration assembly to start the filtration process.
- Collect the filtrate (sample) into the collection flask or other vessel.
- C Replace the filter funnel portion of the assembly when the filter becomes too restricted because of solids buildup on the filter. To replace the filter, depress the pressure/vacuum release button, disconnect the filter funnel and replace it with a new one, create a vacuum with the hand pump, and continue filtering the remaining sample.
- Release the negative pressure at the vacuum pump and in the filtration equipment; disconnect the collection flask.
- Transfer the filtrate from the collection flask into appropriate sample containers, avoiding excessive turbulence or agitation to the sample.
- Preserve the sample as necessary and verify that the pH is sufficient for the criteria.
- C Verify that a PTFE liner is present in the cap. Secure the cap tightly.
- Label the sample bottle with an appropriate label. Be sure to include all necessary information.
- Record the information in the field logbook and field sheet, and complete all chain-of-custody documents (see Instruction F-1, "Documentation," Appendix F).
- Discard or decontaminate all sample filtration equipment and materials in accordance with the project sampling and analysis plan.

E.1.3 Potential problems.

E.1.3.1 One inherent problem associated with the filtration of aqueous environmental samples is the filter becoming clogged. The following are some considerations regarding liquid filtration:

- Always have extra filters available at the sampling site.
- Prefilter dirty samples with a larger pore size filter.
- For highly turbid samples a negative filtration system may be more efficient.
- Avoid pouring sediments from the bottom of the collection flask into the filter funnel.
- When the filtrate flow becomes too slow because of filter loading, change the filter. Avoid increasing the pressure and rupturing the filter membrane.

E.1.3.2 To verify the effectiveness of the decontamination procedures, as well as to evaluate the cross-contamination potential of the filter media, recommend collection of equipment blanks. A detailed discussion of equipment blanks is contained in Instruction G-2 (Appendix G).

E.1.4 Other filtration procedures. The filtration techniques outlined in the preceding paragraphs provide some specifics for filtering various liquid media in the field. Other guidelines for filtration techniques exist, i.e., American Society for Testing and Materials (ASTM). As with any technique, the technical team should consider their project objectives and how their procedure will affect the chemistry of the sample before analysis. Such factors as aeration, agitation, temperature, pressure, adsorption, chemical compatibility, etc., should all be considered.

E.2 Homogenizing Techniques

E.2.1 Scope and application. This instruction provides guidance for homogenizing samples. Proper homogenization is vital to accurately assessing the condition of a particular site. Correct homogenization techniques are also important for preparing the necessary quality control (QC) samples associated with a typical sampling event. Homogenization techniques should not be used when samples for volatile organic analyses (VOA) or other parameters that require undisturbed samples are collected.

E.2.2 Sample handling and mixing. An integral part of any sampling investigation is obtaining samples that truly represent the site under investigation. Therefore, applying proper homogenization techniques will help ensure that conditions are being accurately represented. Generation of field control samples (e.g., replicate samples) provides a means for evaluating matrix heterogeneity and the sampling and handling techniques of field personnel. However, for this evaluation to be meaningful, field sampling personnel must be able to properly homogenize and divide collected samples.

E.2.2.1 Sampling equipment composition. The composition of sampling equipment can affect sample analytical results. Sampling materials used must be properly decontaminated and must not contaminate the sample being collected. The standard materials for sampling equipment used to collect samples for trace organic compounds or metals analyses are given in Table E.1. This table may be used as a guide to select the proper sampling instruments.

Table E.1
Standard Materials for Sampling Equipment

Analysis/Site Condition	Preferred Material
Metals	Glass or PTFE
Organics	Stainless steel, glass, or PTFE
Corrosive Soil/Waste	Glass or PTFE

E.2.2.2 Required sample volumes. The volume of sample obtained should be sufficient to perform all required analyses with an additional amount collected to provide for quality control needs, including any split or replicate samples. The volume of sample required by the laboratory depends on the analyses to be performed. Volumes and containers identified in Appendix B are sufficient volumes for the prescribed analysis. If deviations from these volumes are necessary due to low sample yields, the laboratory receiving the sample and conducting the analyses should be consulted for alternative volume requirements. The volumes of samples collected from waste sources at hazardous waste sites or samples from sources that are known to be toxic should be kept to an absolute minimum since disposal costs of excess sample material are high. The laboratory or project personnel may require that excess sample volume be returned to the site because of the hazardous nature of the samples or because of sensitive political issues surrounding the project. If samples are being collected for bench-scale or pilot-scale remediation studies, larger volumes may be necessary. This scenario normally involves sending large bulk volumes to a laboratory to undergo various applications/manipulations to identify the optimum conditions for remediation of a particular waste stream. The data user (i.e., design engineer) or laboratory should be contacted to determine the volume of material required.

E.2.2.3 Aqueous samples. Aqueous samples are typically considered homogeneous because of the physical properties of water, such as diffusion and the ability to flow and freely mix. Therefore, aqueous samples do not require mixing. However, when solids are present within the aqueous samples, viscous or semisolid liquids are encountered, and the sample will require mixing. These samples can be shaken well

or stirred thoroughly with a tool of appropriate composition. The sampler may also encounter portions of the media that are immiscible with water and separate into distinct phases. In these situations, it is advisable to collect a sample from each layer/phase as well as a homogenized sample. When multiple phases are sampled, the sample should be homogenized in the laboratory to achieve the most homogeneous sample. Water samples (potable well, monitoring well, surface water) should be obtained by alternately filling sample containers from the same sampling device for each parameter. Split and replicate samples will be collected simultaneously with the primary samples. Containers for VOA will be filled first, followed by containers for semivolatile organics, metals, cyanide, and water quality parameters. Each VOA container should be completely filled immediately, rather than splitting the water between bottles and filling the bottles incrementally. The containers will all be filled from the sampling device if possible. If this is not possible, a minimum of two containers (one for the primary sample and one for the split sample) will be filled from each sampling volume. If more than two containers can be filled from one sampling volume, the number of containers filled should be an even number (i.e., two or four) so that an equal number of containers for the primary and split samples are prepared. The remaining portions of the sample will then be prepared by splitting each sampling volume between containers for the primary and replicate samples.

E.2.2.4 Solid samples. Obtaining samples in a soil or sediment matrix requires homogenization of the sample aliquot prior to filling sample containers. However, volatile organic samples are the exception; samples being analyzed for volatile organic compounds (VOCs) must always be taken from discrete locations prior to mixing. Refer to Instruction E-4 for additional information on the collection, handling, and storage of solid VOC samples. This practice is necessary to prevent loss of volatile constituents and to preserve, to the extent practicable, the physical integrity of the volatile fraction. Homogenization of the sample for remaining parameters is necessary to create a representative sample media. Moisture content, sediments, and waste materials may inhibit the ability to achieve complete mixing prior to filling sample containers. Consequently, alternative procedures may need to be pursued, i.e., kneading, particle size reduction (PSR), or particle size separation (PSS). However, it is extremely important that solid samples be mixed as thoroughly as possible to ensure that the sample is as representative as possible of the sample location.

E.2.2.4.1 Before sample mixing is performed, instructions on the removal of extraneous sample materials (grass or materials in “root zone,” leaves, sticks, rocks, etc.) should be given. This can be accomplished by the removal of material by a gloved hand, or through the use of PSS devices (i.e., sieves). Other procedures employed may include PSR techniques. This may be as simple as breaking up large material with a hammer, or may include more elaborate techniques (grinder or mill). However, many of these PSR devices are difficult to decontaminate, and may not be conducive to trace level chemical analyses.

E.2.2.4.2 Homogenization procedures may be accomplished by several methods. The method best suited for the media will depend on the physical characteristics of the solid material (e.g., heterogeneity of media, maximum particle size present, moisture content, etc.). In general, homogenization is accomplished by filling a properly decontaminated container with the sample and mixing it with a decontaminated implement. The container should be large enough to hold the sample volume and accommodate the procedures without spilling. In most cases, the method of choice for mixing is referred to as cone and quartering and can be performed in a bowl or tray of an appropriate material (depending on the analytical parameters to be performed). First all the soils will be disaggregated to less than 6-mm (1/4-in.) diameter as the sample is mixed. The soils are then gathered into a pile in the middle of the container and divided into quarters. Each quarter is mixed, then soils from opposite corners are mixed together again. Soils are then partitioned into quarters again, and this time adjacent corners are mixed together, then the whole combined again. The extent of mixing required will depend on the nature of the sample and should achieve a consistent physical appearance before sample containers are filled. The soils are then divided into final quarters, which are equally subsampled to fill the appropriate containers. If the solid medium is not amenable to cone and

quartering techniques due to the high moisture content or high cohesiveness of the waste, recommend kneading techniques be pursued. First place the sample into a clean noncontaminating bag, and knead materials thoroughly to mix the sample.

E.2.3 Potential problems.

E.2.3.1 The true homogenization of soil, sediment, or sludge samples may be difficult to accomplish under field conditions. However, the homogenizing techniques may be evaluated with the use of a noninterfering dye. The noninterfering dye should be added to the sample medium prior to homogenizing procedures. The resulting distribution of the dye throughout the sample medium during the mixing will indicate the effectiveness of the procedures and areas requiring further mixing.

E.2.3.2 Another important aspect of obtaining a representative sample is to employ proper subsampling techniques. Recommend as a final step of the mixing that the material as a whole be subsampled as equally as possible. This may be accomplished by the procedures already noted or as follows. Flatten the piled material into an oblong shape. Using a flat-bottomed scoop, collect a strip of material across the entire width of the short axis. Repeat this procedure at evenly spaced widths until the sample containers are filled. If the material is cohesive, the solid medium may be flattened, and cut into cubes. Collect random cubes into a subsample, which will be rekneaded and placed into the appropriate sample containers.

E.3 Compositing Samples

E.3.1 Scope and application. This instruction provides information on the various types of composite sampling techniques and the proper procedures to obtain a composite sample. The technique of compositing discrete samples is typically employed when the site under investigation is quite large to improve the precision (lower the variance) of the estimated average contaminant concentrations, especially when contamination exhibits a short-range heterogeneity, and to decrease the probability of making a wrong decision based on limited data. Consultation with data users should be done to determine the appropriateness of applying compositing schemes to meet project objectives. Compositing scenarios that employ a retesting scheme may also be effective in identifying hot spots if a majority of the discrete samples are anticipated to be nondetect and there is adequate sensitivity of the analyses. In this case, the maximum number of discrete samples composited should be determined based on the dilution factor imposed and the sensitivity of the analyses in relation to the project decision level. Compositing schemes are of most benefit when analytical costs are high or analysis is time-consuming relative to sampling costs. Composite sampling may also decrease overall sampling and analytical costs. Composite sampling is not specific to one matrix. Rather it can be utilized for solid, semisolid, liquid, and air matrices.

E.3.2 Compositing techniques. Composite samples consist of a series of discrete grab samples that are mixed together to characterize the average composition of a given material. The discrete samples used to make up a composite sample are typically of equal volume, but may be weighted to reflect an increased flow or volume. Regardless, all discrete samples must be collected in an identical fashion. Likewise, the number of grab samples forming a composite should remain consistent (i.e., a number and pattern for collection of grab samples within a grid should be selected and, for a given grid size, should not be changed). Five types of composite samples are discussed in the following sections.

E.3.2.1 Flow-proportioned composite. Flow-proportional composite samples are collected proportional to the flow rate during the compositing period by either a time-varying/constant volume or a time-constant/varying volume method. This type of sampling is usually associated with wastewater or storm water runoff sampling. To enhance the representativeness of the flow-proportioned composite sample, suggest collection using an automatic sampler that is paced by a flowmeter. Automatic samplers reduce human error, and can directly correlate flow with both sample size and time. Figure E-1a and c illustrate flow-proportioned composite sampling.

E.3.2.2 Time composite. A time composite sample is composed of a varying number of discrete samples collected at equal time intervals during the compositing period. The time composite sample is typically used to sample wastewater and streams, and in some air sampling applications. Time composite samples are typically obtained using automated programmable samplers. When a large number of locations must be sampled, automatic samplers may be set up to sample these locations simultaneously with minimal supervision and costs. In hazardous situations, use of automatic samplers can reduce personnel contact with hazardous waste streams or with potentially dangerous sampling environments. The disadvantages of automatic sampling equipment are its high cost and extensive maintenance requirements. These disadvantages can be offset by reduced labor requirements, proper maintenance, and the proper choice of equipment. When access to the waste stream is relatively easy and sufficient labor is available, manual methods are also quite effective. The most significant disadvantage of manual sampling is that it is labor-intensive, particularly with respect to long-term composite sampling. Figure E-1b illustrates equal time compositing.

E.3.2.3 Areal composite. Areal composite samples are samples collected from individual grab samples collected in an area or on a cross-sectional basis. Areal composites are made up of equal volumes of grab samples where all grabs are collected in an identical manner. Areal composite sampling is typically used for estimating average contaminant concentrations in surface soils or sediments. This is especially

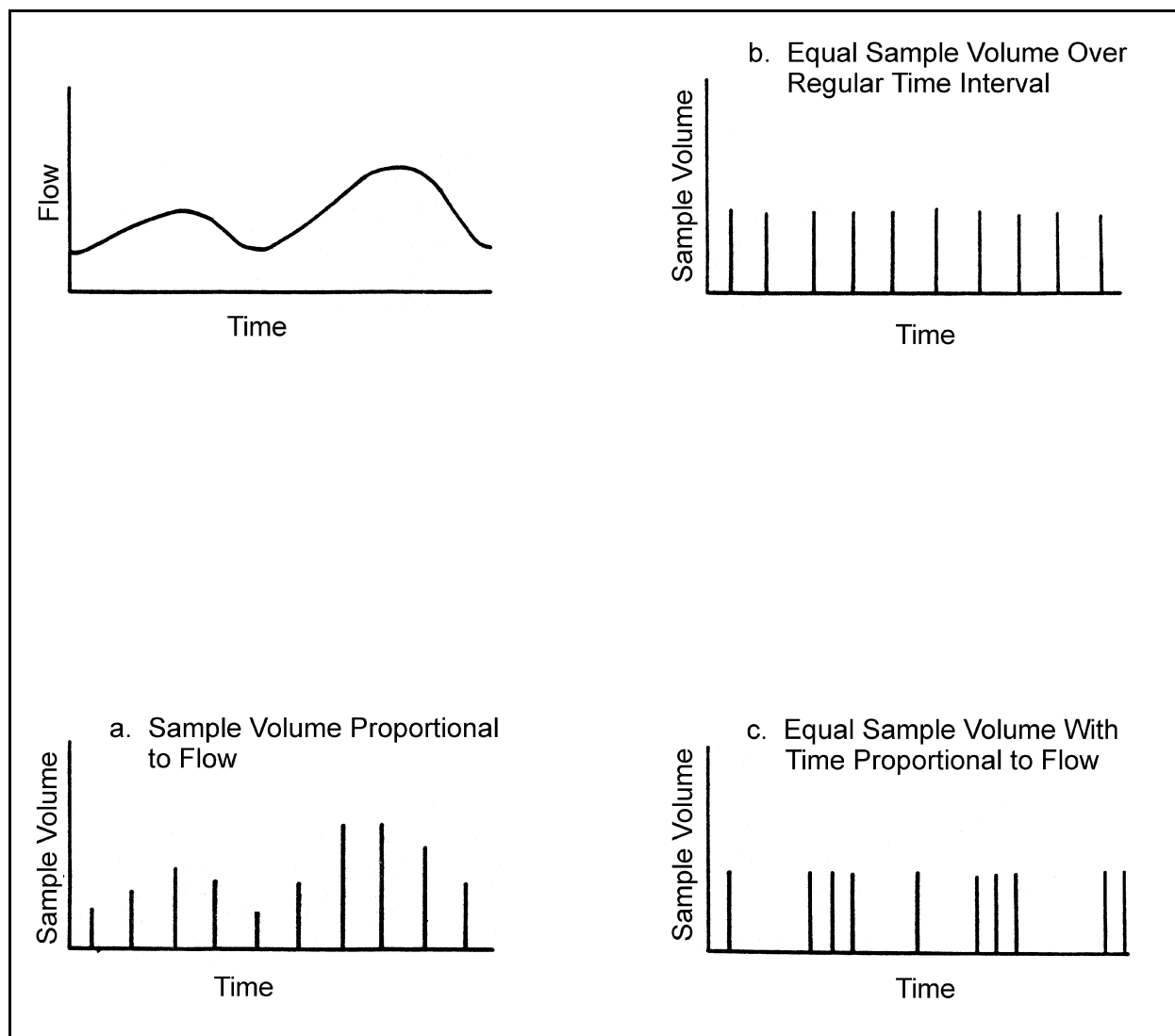


Figure E-1. Composite sampling methods

useful when contaminants are present in a nugget form (i.e., TNT chunks, lead shot, etc.), exhibiting large differences in concentration in a small area (short-range heterogeneity). Grid sizes should be kept moderate (1.5 to 3 m (<5 to 10 ft) in diameter), if project objectives and intended use of the data are to maintain aspects of a “discrete” sample while providing better overall coverage. Reference Jenkins et al. (1996a) for additional details on the use of short range areal composite sampling techniques.

E.3.2.4 Vertical composite. Vertical composite samples are also collected from individual grab samples but taken from a vertical cross section. Vertical composites are also made up of equal volumes of grab samples where all grab samples are collected in an identical manner. Vertical profiles of a soil borehole or sediment columns are examples of vertical compositing.

E.3.2.5 Volume composite. Volume composite samples are collected from discrete samples whose aliquot volumes are proportional to the volume of sampled material. This type of composite is usually

associated with hazardous waste bulking operations, where the composite sample is intended to represent the combined or bulked waste. Discrete samples are typically combined within a group of compatible wastes to undergo physical and chemical testing to define disposal options or determine acceptability at a treatment, storage, and disposal facility.

E.3.3 Compositing grab samples. In general, compositing grab samples lends itself to lowering analytical costs because it reduces the number of analyses. Collecting composite samples also requires project-specific decisions for several key points, including the type of composite sampling technique that will meet the project needs (i.e., time composite, areal composite, etc.); the total number of composite samples needed; the number of grab samples in each composite; and the size and pattern of the sampling grid. These issues may depend on the size of the area under investigation, the nature of the contaminants, and the position of the regulators. Good documentation of sampling locations is also essential in all field sampling, particularly when several grab samples are being homogenized to form a composite. If a contaminant is detected in a composite sample, each of the discrete grab samples that made up the composite should be analyzed individually to determine the actual distribution of the contamination. Procedures should be established between the project manager and the laboratory to ensure that holding times for the discrete grab samples are not exceeded. However, caution should be exercised when reviewing this type of confirmatory analysis due to the lag time between sample analyses and expiration of the holding times of the samples.

E.3.3.1 Solid matrix. Composite samples should be prepared as follows:

- Collect discrete grab samples using the appropriate instructions as outlined in Appendices C and D. To obtain a representative composite sample, it is important that all grab samples are collected in identical fashion.
- Homogenize the individual discrete samples as outlined in Instruction E-2, and place them into properly labeled sample containers.
- Assemble the sample containers that contain the grab samples that will make up a specific composite sample.
- Remove an appropriate volume of discrete sample (aliquot) from each sample container and place it into a clean stainless steel mixing bowl. Each aliquot amount should be taken in an identical fashion to facilitate representativeness. Avoid generating excess contaminated soil when possible.
- Homogenize the aliquots as described in Instruction E-2.
- Remove sample amounts from the homogenized composite sample and place them into the proper containers for shipment to the laboratory.
- Place the individual homogenized discrete samples in proper storage conditions after aliquots are removed for compositing, when a retesting scheme is employed, or if it is of benefit to the project. If the composite sample results do not appear to be accurate or if evidence of contamination exists, subsequent analyses of the individual grab samples that composed the composite may confirm the results and provide discrete information.

E.3.3.2 Liquid matrix. The preparation of liquid matrix composite samples is typically easier than that of solid matrices due to the tendency of liquids to homogenize easily. Also, it is common practice to send liquid grab samples to the laboratory for compositing because of the difficulties in handling larger sample volumes (4 to 16 L (1 to 4 gal) for a typical wastewater sampling event) and to minimize the potential

to introduce contaminants. When liquid composite samples are to be generated in the field, the following procedure should be used:

- Assemble all sample containers that contain the grab samples that will make up a specific composite sample.
- Shake or stir the individual containers to homogenize.
- Using clean glass or disposable pipets, deliver aliquots of the homogenized grab samples directly into a sample container to be sent to the laboratory. (It will require five 200-mL (7-fl-oz) aliquots from five discrete grab samples to generate a 1,000-mL (33-fl-oz) composite sample).
- Seal the container and shake well to mix. Avoid stirring samples if possible to lower the potential of introducing contaminants.
- At some sites it may be beneficial to save and store the individual homogenized grab samples after aliquots are removed for compositing. If the composite sample results do not appear to be accurate, subsequent analyses of the individual grab samples that composed the composite may confirm the results. Confirmatory analyses of these samples would likely be for informational purposes only since the holding times of the samples may have expired.

E.3.4 Potential problems.

E.3.4.1 Compositing does not allow the spatial variability of contamination or discrete information to be determined. Additional analyses of the individual grab samples are required.

E.3.4.2 Low concentrations of contaminants in individual grab samples may be diluted so that the total composite concentration is below the detection limit. In this case, the existence of the contamination in individual samples would go unnoticed. Therefore, the maximum number of discrete samples composited should be based on the dilution factor from the compositing and the analytical sensitivity in comparison to the project decision level and sensitivity requirements.

E.3.4.3 When the sampled medium is not amenable to mixing techniques (samples are moist and clayey), it may be very difficult to create a homogeneous sample mixture. Consequently, the resulting composite may not represent an average of all the grabs.

E.3.4.4 Compositing techniques should not be employed when chemical interactions may diminish the integrity of the sample (i.e., VOC samples).

E.3.4.5 Compositing schemes are not efficient when the goal is to identify hot spots and there is a high probability that the discrete samples contain detectable concentrations. The amount of retesting may be significant to achieve the objectives.

E.3.4.6 Compositing schemes are not efficient if analytical costs are low.

E.3.4.7 Obtaining samples by an automatic sampling device is typically difficult for the first-time user. However, after the sampler has become familiar with the sampling device and any problems have been addressed, these devices prove to be quite reliable.

E.4 Collection, Handling, and Storage of Solid Samples for VOC Analysis

E.4.1 Scope and application.

E.4.1.1 This instruction presents guidance for the collection and handling of surface/subsurface sediments, soils, and solid hazardous waste materials taken for VOC characterization. The procedures include collection, handling, storage, and onsite preparation for analysis of discrete samples; and collection, handling, and storage of discrete samples for offsite sample preparation. Information concerning the selection and application of the sampling devices available for subsurface bulk sample collection can be found in Instructions C-5 and C-6, Appendix C, and Instruction D-1, Appendix D.

E.4.1.2 Special procedures are necessary for VOCs, since in most solid matrices these analytes coexist in gaseous, liquid, and solid (sorbed) phases. Loss of analyte from any one phase may render the sample unrepresentative of the material as a whole. Therefore, sample collection, handling, and analysis must be performed under conditions that maintain the accountability of VOCs in all phases. In general, uncontrolled VOC losses occur through two mechanisms: volatilization and degradation. Volatilization losses occur whenever gaseous molecules are allowed to move away freely. This loss mechanism usually dominates whenever a new surface is created. Traditional sampling procedures used for acquisition of solid VOC samples are very susceptible to this type of loss. Further losses during transport and storage are common if fine soil grains are present on the threads of the vial or at sealing surfaces, thereby preventing a good seal. The most significant VOC losses, however, are due to the reopening of the vial and sample handling at the laboratory. In general, the extent to which VOCs are lost will depend on the vapor phase concentration (analyte vapor pressure), extent of surface area exposure, length of exposure, and porosity of the sample matrix. However, studies have shown VOC losses of a magnitude 10X and higher are common. Degradation losses are usually attributable to biological processes. Aerobic biological degradation dominates, because traditional intrusive collection methods expose the sample to oxygen in the atmosphere. The rate of biological degradation depends on several factors, including the indigenous microbiological population, chemical properties of the VOC, nutrients, moisture, and temperature. Aromatic compounds are quite susceptible to this loss mechanism, and preservation by cooling to $4^{\circ}\text{C} \pm 2^{\circ}\text{C}$ has been found to be insufficient in retarding biological degradation.

E.4.1.3 Solid sample preparation for VOC analysis is typically performed by vapor partitioning (i.e., purge-and-trap or headspace), or by methanol extraction. Refer to Method 5035, EPA/SW-846, for these sample collection procedures. In general, when VOC analysis is performed by gas chromatography or gas chromatography/mass spectrometry, vapor partitioning methods are used for solid samples thought to be contaminated with VOCs at levels lower than 0.2 mg/kg (Method 5035, low-level method). In contrast, solid samples thought to have concentrations above 0.2 mg/kg are analyzed after extraction (dilution) with methanol (Method 5035, high-level method). Method 5035 has been designed to improve the sample handling and preservation procedures and minimize the negative bias in VOC results by incorporating several preparatory steps traditionally performed in the laboratory into the field. These sample collection procedures differ significantly from traditional methods and impact several technical personnel in both the field and laboratory. These changes require increased coordination and communication between parties involved to ensure successful acquisition of representative solid VOC samples. The procedures discussed in this instruction are for clarification and implementation of SW-846 Method 5035, and are designed to limit sample VOC losses by volatilization and biodegradation. This is accomplished by stressing that samples are collected only from freshly exposed surfaces, sample collection and transfer are performed quickly and in a nondisruptive fashion whenever possible, sample procedures follow Method 5035 low-level (purge and trap), or high-level (methanol) extraction procedures, or samples are taken in an airtight vessel cooled to $4^{\circ}\text{C} \pm 2^{\circ}\text{C}$, and are held up to only 48 hours prior to analysis. It is important to recognize that Method 5035 low-level (closed-system purge-and-trap) procedure requires the laboratory to have special equipment

designed to handle VOA vials in an automated sample introduction system. Furthermore, these methods of analysis do not necessarily apply to water-soluble VOCs. For information concerning the analysis of water-soluble VOCs, refer to SW-846 Method 5000.

E.4.2 Sampling strategy and number of samples.

E.4.2.1 In general, the selection of methodology — low-level versus high-level method — will depend on project data quality objectives (DQOs) (action or decision levels), and the expected VOC concentrations of the environmental matrices to be sampled. This is illustrated in the flow chart in Figure E-2. As shown in Figure E-2, the high-level method is used when VOC action levels are relatively high or the VOC concentrations are greater than 200 : g/kg. The low-level method is used when project action levels are low, or site VOC concentrations are less than 200 : g/kg. When action levels are low, field screening should be performed to direct the acquisition of either low-level or high-level samples. Recommend the field screening be performed by onsite gas chromatography, or according to procedures described in Hewitt and Lukash 1997. If no field information is available, both low-level and high-level samples must be collected. The collection of both low-level and high-level samples for fixed-laboratory analyses constitutes the most conservative approach to avoid the need for remobilization/resampling efforts to obtain necessary data.

E.4.2.2 Screening techniques at the laboratory are also recommended to confirm any onsite results and to avoid damage to laboratory instrumentation. If no onsite or laboratory screening is performed, and both low-level and high-level samples are submitted to the laboratory, the laboratory should perform the high-level analyses first, and if no VOCs are detected, analyze the corresponding low-level sample. If the low-level sample is analyzed initially without further information, the laboratory runs the risk of contaminating the analytical system (requiring significant maintenance) and potentially impacting data of other samples within that analytical batch. Reanalysis using appropriate preparatory procedures is necessary for any samples that exceed the calibration range of the instrument.

E.4.2.3 Regardless of the methodology employed, several collocated samples will generally be required for each sample location (e.g., from each sampling depth or soil boring). The exact number of required collocated samples will depend on several factors, including analytical methodology (the high-level versus the low-level method), field screening results, the laboratory's protocols for screening of samples, and project requirements for field QC samples (e.g., matrix spikes and duplicates). For example, when low-level analysis is required and field screening results show site VOC concentrations to be low, at least two samples must be collected for analysis. Two samples are necessary due to the entire vial being processed during the VOC analysis. The second vial allows the laboratory an opportunity to perform an additional low-level analysis should the first analysis be unacceptable. When low-level analysis is required and the site VOC concentrations are unknown, at least two samples must be collected for potential low-level analysis and one sample must be collected for potential high-level analysis. The high-level sample is subsampled and the aliquot of methanol extract diluted for VOC analysis. Therefore, one high-level sample can accommodate multiple high-level analyses. Finally, if the laboratory plans to screen the samples, an aliquot of the high-level sample may be used, or an additional sample may be collected.

E.4.2.4 For acquisition of QC samples, field screening information becomes even more important. In order to avoid the need to collect both low-level and high-level QC samples, field screening should be performed, or alternative collection procedures (i.e., EnCore™) employed for these QC samples. For example, the field duplicate typically requires one additional collocated sample, while the matrix spike/matrix spike duplicate requires an additional two samples. However, if no information on site VOC concentrations is available, this could expand to three samples for the field duplicate (two for low-level and one for high-level), and six additional samples for the matrix spike/matrix spike duplicate. In addition to the samples

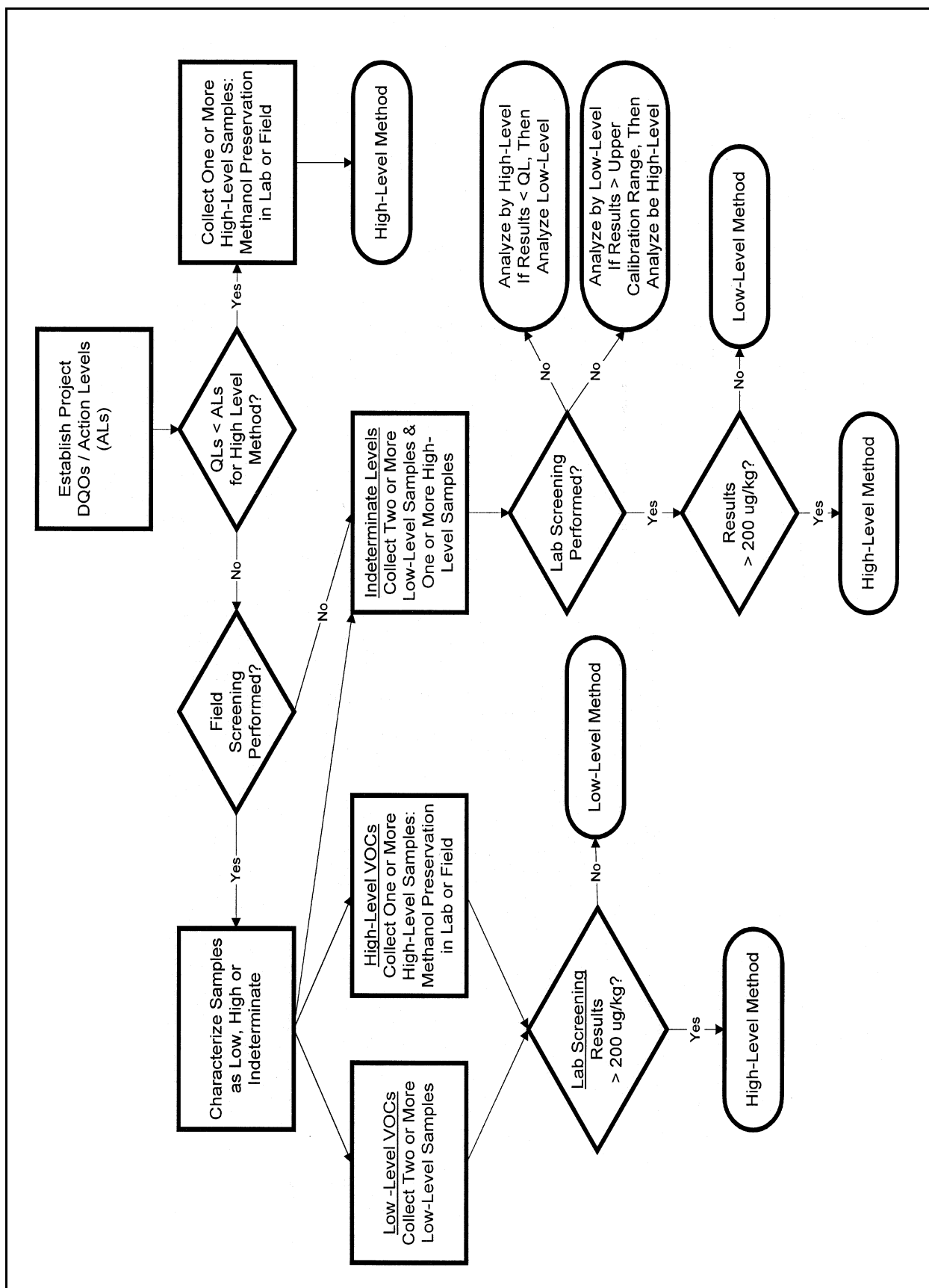


Figure E-2. VOC analysis decision tree

collected for VOC analysis, another collocated sample must be collected for a moisture content determination in order to report the VOC results on a dry-weight basis. Samples for moisture content determinations may be collected in conventional VOA vials and cooled to $4\text{ }^{\circ}\text{C} \pm 2\text{ }^{\circ}\text{C}$. Proper project coordination between field and laboratory personnel and implementation of onsite and/or laboratory screening processes can help reduce the numbers of samples to manageable quantities.

E.4.3 Sample collection summary. In order to minimize VOC losses, Method 5035 sample collection and preparation procedures dramatically modify both the low-level and high-level VOC methods. The revised sample collection techniques greatly reduce the time in which samples are exposed to atmospheric conditions. Initially to help maintain the physical structure of samples of a cohesive granular material, a hand-operated coring device must be used to collect the appropriate sample size for laboratory analysis (e.g., cylindrical soil columns are extruded into vials using disposable plastic syringes with the tapered front ends removed). However, some materials (e.g., cemented or noncohesive granular material) may be too difficult for coring tools to penetrate or contain. These materials can be sampled by fragmenting a larger portion of the material with a clean chisel to generate aggregate(s) of a size that can follow sampling protocol 2 (placed into a VOA vial or bottle containing chemical preservative). When aggregate(s) are transferred, precautions must be taken to prevent compromising the sealing surfaces and threads of the container. Losses of VOCs using this procedure are dependent on the location of the contaminant relative to the surface of the material being sampled. Therefore, caution should be used during data interpretation. As a last resort when this task cannot be performed onsite, a large consolidated sample can be collected in a vaportight container and transported to the laboratory for subsampling. Sample protocol 2 presents a sample being added to collection vials containing chemical preservatives such as sodium bisulfate solution or methanol for the low-level and high-level methods, respectively. Field personnel transfer samples immediately into preweighed vials containing chemical preservatives without additional sample handling. The vials and chemical preservative are weighed in the field before use, and are reweighed after the sample aliquot addition to obtain the net sample weight. Alternatively, samples for both the low-level and high-level methods may be collected following sample protocol 1. Sampling is performed with a coring device, which becomes the sample container and is hermetically sealed (e.g., EnCore™ sampler from En Chem, Inc.) and stored at $4\text{ }^{\circ}\text{C} \pm 2\text{ }^{\circ}\text{C}$ for a maximum of 48 hours.

E.4.3.1 Sampling protocol 1.

E.4.3.1.1 Sampling protocol 1 consists of a coring device that also serves as a shipping container. Presently, the EnCore™ sampler is the only commercially available coring device that was designed to collect, store, and transfer soils with minimal loss of VOCs. The disposable EnCore™ sampler is designed to be a single-use coring device that stores the soil sample in a hermetically sealed, headspace-free containment that maintains sample integrity. Most soils that require sampling will consist of cohesive granular materials, which allow the use of such a coring device. However, the sampling protocol will not be applicable to all solid environmental matrices. Some geological materials are impossible to core (e.g., gravels and hard dry clays). Refer to sampling protocol 2 for guidance on handling these materials. The EnCore™ sampler has a hand-operated coring tool available for obtaining 5-g and 25-g samples. The 25-g sampler is designed for the zero headspace extraction for purposes of the VOC Toxicity Characteristic Leaching Procedure testing. Note that the 25-g sampler should not be used to collect, store, and transfer soils from the field for subsampling in the laboratory into 5-g aliquots. This additional sample handling would defeat the benefit that the EnCore™ sampler affords.

E.4.3.1.2 Advantages of sampling protocol 1 include the simplified field procedures, which do not require sample weighing or addition of preservatives in the field. Because sample preparation is performed at the laboratory, exposure hazards and Department of Transportation (DOT) shipping issues arising from

the field application of chemical preservatives such as methanol are also avoided. However, samples must be stored at $4\text{ }^{\circ}\text{C} \pm 2\text{ }^{\circ}\text{C}$ and prepared for analysis within 48 hours of collection. The short holding time for sample preparation usually requires additional coordination with the analytical laboratory and may involve higher analytical costs. The following is general guidance for the collection of a soil sample using the EnCore™ sampler:

- After the split spoon is opened and a fresh surface is exposed to the atmosphere, the sample collection process should be completed in a minimal amount of time with the least amount of disruption (disaggregation) as possible. Visual inspection and an appropriate screening method (e.g., photoionization detector or flame ionization detector readings) may be selected to determine the interval of the soil core to be sampled.
- Rough trimming of the sampling location surface layers should be considered if the material may have already lost VOCs (been exposed for more than a few minutes) or if it may be contaminated by other waste, different soil strata, or vegetation. Surface layers can be removed by scraping the surface using a clean spatula, scoop, or knife.
- Insert the clean coring tool into a fresh surface for sample collection. Take care not to trap air behind the sample. An undisturbed sample is obtained by pushing the barrel of the coring tool into a freshly exposed surface and removing the corer once it is filled.
- The exterior of the barrel should be quickly wiped with a clean disposable towel to ensure a tight seal and the cap snapped on the open end.
- The sampler should be labeled, inserted into the sealable pouch, and immediately cooled to $4\text{ }^{\circ}\text{C} \pm 2\text{ }^{\circ}\text{C}$.
- Repeat this procedure to collect separate collocated samples for moisture content and any QC samples.
- Prepare the shipment to go to the laboratory. If samples are going to be shipped near the weekend or holiday, recommend coordinating with the receiving laboratory to ensure holding time of 48 hours for the EnCore™ sample is met.

E.4.3.2 Sampling protocol 2.

E.4.3.2.1 Sampling protocol 2 is applicable to all solid matrices. However, if soils are not retained within the coring device (i.e., wet enough to flow), it may be necessary to cover the open end of the coring device with aluminum foil in a manner that will maintain sample integrity until the material is transferred to appropriate sample vials. When gravel, or a mixture of gravel and fines, that cannot be easily obtained using coring tools is sampled, a sample may have to be transferred using a clean spatula or scoop. The collection vial will contain the chemical preservative; therefore, samples should be dislodged with minimal splashing and without the spatula or scoop contacting the liquid contents. For some solids, a wide-bottom funnel or similar channeling device may be necessary to facilitate transfer to the container and prevent compromising the sealing surfaces of the container. Losses of VOCs are likely because of the additional sample handling and the noncohesive nature of the material, which exposes more surface area to the atmosphere. Another potential source of error during the subsampling process is the separation of coarser materials from fines, which can skew the concentration data if the VOC contamination is associated with particular particle sizes, which are not properly represented in the sample. Also, due to an aqueous acidic

solution of sodium bisulfate being used to preserve samples for the low-level analyses, samples must be tested for carbonate interferences in the field before the samples are containerized. If carbonates are present, the sodium bisulfate may potentially react with the carbonates producing effervescence, which promotes the loss of VOCs. The high-level method is not affected by the presence of carbonates. In these cases, alternative procedures (i.e., EnCore™ or high-level method) should be used. All sampling difficulties should be well documented in field logbooks and caution used in the interpretation of the data obtained from these types of materials. Finally, recommend the field personnel become familiar with the volume of material needed to reach the estimated 5 (or project-specific) grams. For cohesive soils, recommend approximating a mark on the disposable syringes to help guide the acquisition of the soils needed. For other materials, preweighing materials to the volume needed, which are then discarded, will help visualize the amount of material to be transferred when sampling time and sample handling are critical.

E.4.3.2.2 All of the sample containers used should be made of glass and have a thick septum cushion between the sealing material (PTFE) liner and cap (rigid plastic screw cap or aluminum crimp top). PTFE-lined caps for bottles should have flexible septum backing and be at least 10 mils thick to ensure a liquid or airtight seal. The sample containers (VOA vials) containing appropriate volume and grade (e.g., purge-and-trap grade methanol) chemical preservative should be prepared by the laboratory prior to shipment to the field. Surrogate compound(s) may be added by the laboratory at this time to allow an assessment of the sampling procedures. The laboratory should be responsible for providing trip blanks and ambient blanks (e.g., methanol). Note that the sample vials for the Method 5035 low-level method are designed to be placed directly on the laboratory's instrument (i.e., auto sampler) so that they remain within the closed system up to and during VOCs analysis. Therefore, it is critical that only the 40-mL VOA vial (and not the 60-mL VOA vial) containing the magnetic stir bars be used for the low-level analysis. Recommend that disposable stir bars be used since memory effects have been reported with magnetic stir bars that have been reused without effective decontamination. Recommend the laboratory note the tare weight of the sample vial with preservative (and stir bar, if necessary) on the sample label before sample vial shipment. After this initial weighing, sample containers should be opened only to transfer sample into them. After the sample transfer into the collection vessel, the sample container is reweighed in the field (and again in the laboratory prior to analyses). The difference in the weight, measured before and after the sample is introduced, is used to establish the sample wet weight. Any discrepancies between field weights and laboratory weights must be thoroughly documented to assess the loss of sample or extract and the acceptability of the sample for analysis as outlined in Section E.4.4.1. The following is general guidance for the collection of soil samples for field preservation for Method 5035 low-level or high-level methods.

- Solid matrices should be screened for carbonates. Refer to Section E.4.3.2.1 if carbonates are present.
- Field personnel should record the weight of the sample vials containing preservative to verify consistency with the laboratory tare weight and ensure no loss during initial transport of the sample containers to the field. Note any discrepancies back to the laboratory and in the field logbook.
- The coring device should be prepared as follows: cut off tapered front end of a disposable plastic syringe and remove the rubber cap from the plunger. A mark may be placed on the syringe to approximate the volume of material needed.
- After the split spoon is opened and a fresh surface is exposed to the atmosphere, the sample collection process should be completed in a minimal amount of time with the least amount of disruption (disaggregation) as possible. Visual inspection and an appropriate screening method

(e.g., photoionization detector or flame ionization detector readings) may be selected to determine the interval of the soil core to be sampled.

- Rough trimming of the sampling location surface layers should be considered if the material may have already lost VOCs (been exposed for more than a few minutes) or if it may be contaminated by other waste, different soil strata, or vegetation. Surface layers can be removed by scraping the surface using a clean spatula, scoop, or knife.
- Insert the clean coring tool (e.g., prepared disposable syringe) into a fresh surface for sample collection. Take care not to trap air behind the sample. An undisturbed sample is obtained by pushing the barrel of the coring tool into a freshly exposed surface and removing the corer once it is filled.
- Hold the vial or bottle containing chemical preservative at an angle when extruding the sample into the container to minimize splashing.
- Perform a visual inspection of the lip and threads of the sample vessel. Remove any foreign debris with a clean towel and cap the vial.
- Tap the vial gently while holding it in an upright position. The purpose of the agitation is to ensure that the preservative completely contacts the soil surfaces and disaggregate any large clumps. The sample vials should not be shaken vigorously or up and down.
- Measure and record the weight of each container into the field logbook and in documentation to the laboratory. Calculate the difference in weight of the container, measured before and after the sample is added, and use to determine the sample wet weight.
- Each of the samples should be immediately placed into smaller sealable plastic bags, collected within a larger plastic bag, placed inside a cooler in an upright position, and cooled to $4^{\circ}\text{C} \pm 2^{\circ}\text{C}$. Because of packaging constraints for shipping (e.g., need for inner receptacles), it is absolutely critical that samples be prechilled to $4^{\circ}\text{C} \pm 2^{\circ}\text{C}$ prior to shipment.
- Repeat these procedures to collect separate collocated samples for moisture content and any QC samples.
- The samples are then prepared for shipment to the laboratory following the criteria and regulatory considerations described in Instruction F-2 of Appendix F.

E.4.4 Potential problems.

E.4.4.1 Field weighing. When field personnel collect samples using sampling protocol 2, they essentially perform the following activities for both the low- and high-level methods. Field personnel must weigh the vials containing the chemical preservatives (e.g., aqueous sodium bisulfate for the low-level and methanol for the high-level method), collect the samples using some type of coring device (e.g., a syringe with its tip removed), extrude the sample cores into the vials, and reweigh the filled vials (to determine the sample wet weight for analysis). A net sample weight of about 5 g is required (assuming a soil density of 1.7 g/cm^3 , this corresponds to a soil volume of about 3 cm^3). According to Method 5035, weights may be made in the laboratory and/or field. If weights are recorded in both locations, this information may be used to track any loss of sample or preservative. If field weight measurements are used, a loss of up to 0.2 g is

allowed for the vial to be considered acceptable for sample analysis. To the extent possible under field conditions, sample containers should be weighed and samples collected in a “protected” environment to permit accurate weighing and handling. Weights should be recorded to the nearest 0.1 g (or 0.01 g if balance allows) for both the low-level and high-level samples. In addition, the meniscus of the chemical preservative may be marked on the sample container to aid in the evaluation of evaporation, accidental spillage in the field, or loss during shipment. Any sample container that shows a loss of methanol (e.g., meniscus below the line marked by the lab) should be discarded.

E.4.4.2 Chemical interactions. Although not substantiated, there have been two occurrences with methanol and sodium bisulfate preservation that require discussion. In the first case, soils that contain aluminum silicates may act as a catalyst causing the conversion of methanol to acetone. The possible mechanism for this interaction is being researched. In the second case, soils like lignite or peat contain a polymeric constituent known as humic acid that may also interact with sodium bisulfate to form acetone. Until either of these two mechanisms can be confirmed or denied, projects should evaluate the potential for acetone to be a site contaminant. For example, if acetone is not an analyte of concern, then the issue may not impact project decisions. However, those projects that cannot remove acetone from the analyte list should be aware of these possible interactions and any acetone detects should be evaluated. A logical source of acetone contamination is the laboratory. Therefore, site-specific sources should always be assessed and not necessarily attributed to one of these interactions.

E.4.4.3 Shipping concerns. DOT shipping requirements need to be taken into account for the preservatives used. Depending on the quantity and method of packaging, sodium bisulfate and methanol may be DOT hazardous materials and subject to DOT hazardous materials regulations. Refer to Instruction F-2, Appendix F, for additional information.

E.4.4.4 Site safety concerns. Methanol is a toxic and flammable liquid. Therefore, methanol must be handled with all safety precautions related to toxic and flammable liquids. Inhalation of methanol vapors must be avoided. Vials should be opened quickly during the sample preservation procedure. Methanol must be handled in a ventilated area. Protective gloves should be worn when vials containing methanol are handled. Methanol should be stored away from open flames, areas of extreme heat, and other ignition sources. Vials containing methanol should be refrigerated (e.g., stored in coolers with ice). Sodium bisulfate is a strong mineral acid and must be handled with all safety precautions related to acids. Contact with the skin and eyes should be avoided. Protective gloves and eye protection should be worn with vials containing sodium bisulfate.

E.4.4.5 Preservative. When samples are preserved with methanol in the field, it is especially critical to avoid the introduction of contamination from external sources such as vehicular emissions or dust. Hence, when samples are preserved with methanol in the field, a methanol blank should be exposed to field conditions during the sample collection process.

E.4.4.6 Boiling point. Sampling protocol 1 using the EnCore™ sampler has not been demonstrated for compounds with boiling points less than 30 °C (e.g. bromomethane, chloroethane, chloromethane, or vinyl chloride).

E.4.4.7 Costs. Significant analytical costs may be incurred due to the level of redundant analyses (both high-level and low-level) when no site VOC concentrations are known. Recommend implementation of screening procedures at the field and/or laboratory to reduce these costs.

E.5 Laboratory Subsampling

E.5.1 Scope and application. This instruction provides direction on how to obtain a representative aliquot of sample for laboratory analysis. Obtaining this aliquot is referred to as laboratory subsampling and is performed by laboratory personnel during sample preparation steps. Current SW-846 and other standard reference methods provide little or no guidance within their preparatory methods for these critical procedures. For this reason, this instruction addresses subsampling techniques for solid, liquid, and multiphased matrices to be used by all laboratories to ensure consistency in subsampling techniques and in the resulting data. It should be noted that specific samples may require special techniques due to problematic matrices or project-specific requirements. Project-specific guidance should be obtained from appropriate project documentation (i.e., Quality Assurance Project Plan) or technical personnel. Good analytical techniques are also required during all subsampling procedures to obtain representative subsample aliquots, minimize potential bias, and accurately assess any contamination at the site. Procedures for the acquisition of soil samples for VOA sample analysis are not included here. Refer to Instruction E-4 of this appendix for information on these procedures.

E.5.2 Subsampling procedures. It is common for many analytical methods to require only a portion of the submitted sample to be subjected to the actual analysis. Excess sample volume is desirable when there is a potential that the sample will need to be reanalyzed. Because only a portion of the submitted sample is actually involved in the evaluation of the sampling location, it is important that the subsample be truly representative of the entire sample submitted. In general, subsampling techniques are distinguished by the analytical method requirements, the distribution of the contaminant within the sampled medium, and the state or condition of the aliquot to be tested. Information covering these topics are routinely available to the laboratory for all except for the contaminants distribution within the evaluated media. Therefore, unless information exists to the contrary, the laboratory should assume the contamination is distributed throughout the laboratory samples. Due to the impact of each sample on the procedures used, recommend that subsampling procedures be continuously reevaluated based on the individual matrix under assessment, subsequent analysis to be performed, and the intended use of resulting data (if known). When project DQOs dictate alternative procedures to those outlined in the following subsections, recommend project subsampling instructions be submitted along with samples to outline proper procedures to be employed. If no project instructions are provided, the following guidance should be used to establish appropriate subsampling practices. Environmental samples, which are not considered undisturbed, should be homogenized prior to arrival at the laboratory. However, laboratory personnel should not assume these samples are properly homogenized in the field. In addition, both solid and liquid matrices experience settling or phase separation during transport. Therefore, it is critical that submitted samples be properly homogenized prior to subsampling when appropriate for the analysis. Techniques used to homogenize or rehomogenize samples should be documented and executed in accordance with the guidance presented in Instruction E-2. Initial inspection of each sample to determine the sample phases, such as liquid, solid, or a combination (multiphase), is critical. Laboratory personnel should document the physical appearance of samples upon receipt, including comments about settling and phase separation. Based on the outcome of this assessment, the following procedures should be used to outline general guidelines for subsampling a variety of matrices.

E.5.2.1 Solid matrix. Soil, sediment, homogeneous and heterogeneous solid substances, concrete, paint chips, ash, etc., are to be subsampled for nonvolatile analyses according to the following guidelines. Procedures for the acquisition of soil samples for VOA sample analysis are not addressed. Refer to Instruction E-4 for information on these procedures. When solid matrices are subsampled, a decision must be made as to whether a representative subsample can be obtained without prior sample manipulation. This depends on whether the sample is homogeneous or heterogeneous in nature, as determined by visual inspection of the physical attributes of the sample, and on determining the sample particle size distribution. Particle size is

the physical dimension of the individual parts (i.e., grains of soil) of the sample. Then consider the following questions:

- C Is there a significant amount of oversized material (be it either naturally occurring (rocks) or artificially introduced material (debris))? Is this material intended to be included/excluded?
- C Are the contaminants present on a molecular scale or macroscale? For instance, are there obvious chemical inclusions (e.g., lead shot, metal chunks, tar balls, solid chemical material (grayish-white explosives)) indicating a macroscale contamination, or is contamination due to a spill/discharge that adsorbed onto individual soil particles indicating a molecular- scale contamination. Contamination on a macroscale is more susceptible to bias during subsampling procedures. Therefore, project-specific instructions (e.g., compositing scheme) should be formulated based on the purpose of the data. Refer to Instruction E-3 for additional information on this application.
- C Does the sample tend to segregate into various size fractions easily? Can they be mixed to produce an even distribution prior to subsampling, or do these fractions need to be physically separated and subsampled individually for recombination into an appropriate sample aliquot?
- C Does the sample maximum particle size meet the minimum allowable class size (as measured by U.S. Standard sieve mesh) as noted in Table E-2, as determined by the subsample mass taken?

Table E-2 Maximum Particle Size Allowed for Subsampling Solid Materials

Subsample Mass (g)	Maximum Particle Size Allowed (cm)	U.S. Standard Sieve Mesh	Wentworth Size Class
0.5 - 1	0.1	18	Coarse sand
2 - 5	0.17	12	Very coarse sand
10	0.21	10	Granule gravel
30	0.31	7	Granule gravel
50	0.37	6	Granule gravel
100	0.46	5	Pebble gravel

If conditions indicate that the sample medium is not homogeneous or that a problem may exist, additional measures may be necessary to obtain a representative sample. These may include techniques for PSR, PSS, sample homogenization, or increasing the size of the sample aliquot taken for analysis. Determining what procedures should be employed may require communication with the data user. Another important aspect of subsampling depends on the method of analysis and the size of the aliquot being taken. Analysis requiring smaller (1-2 g) aliquots (metals, explosives, etc.) requires special considerations so as not to bias the small sample size compared with analysis requiring larger (30 g, extractable organics, or 100 g, toxicity characteristic leaching procedure) analyses. In general, PSR is necessary when the maximum particle size present within the sample is larger than the recommended maximum particle size based on the mass (amount) of the sample aliquot taken for analysis. PSS techniques (sieving) should be performed after PSR, to ensure the desired particle size has been achieved. If PSR (i.e., grinding or milling) or PSS (i.e., sieving) techniques are used, care should be taken to implement the appropriate quality controls, i.e., appropriate inspection and decontamination of devices, to ensure that samples are not contaminated or cross-contaminated during their use.

E.5.2.1.1 Procedures for subsampling homogeneous materials for nonvolatile analyses.

- C Allow the sample and container to equilibrate to room temperature before opening the container.
- C Visually inspect and document the appearance of the sample prior to subsampling.
- C Samples received in brass liners or sections of brass liners must first be extruded onto laboratory tray or pan and mixed as described in the following paragraph.
- C Even if the material received appears homogeneous, the entire sample should be thoroughly mixed using an inert, noncontaminating spatula or rod material by the procedures outlined in Instruction E-2. This may be performed within the original sample container. However, it is more effective and recommended that the material be transferred onto a laboratory tray or pan.
- C For cohesive material, the bulk material should first be reduced in size using a stiff-bladed utensil such that the average size of any clump is approximately pea-sized (approximately 6 mm). If the solid medium is not amenable to these techniques due to the high moisture content or high cohesiveness of the waste, recommend using kneading techniques presented in Instruction E-2.
- C To prepare the subsample, flatten the piled material into an oblong shape. Using a flat-bottomed scoop, collect a strip of material across the entire width of the short axis. Repeat this procedure at evenly spaced widths until the sample aliquot needed is obtained.
 - Alternatively, the sample should be subdivided (quartered) and approximately equal portions removed from each quarter of the sample for inclusion into a final sample aliquot that will be accurately weighed into a clean glass beaker or similar container and analyzed.
- C If the material is cohesive, the solid medium may be flattened and cut into cubes. Collect random cubes into a subsample that will be reknaded and placed into the appropriate sample containers.

E.5.2.1.2 Procedures for subsampling heterogeneous materials for nonvolatile analyses.

- C With heterogeneous material a decision must be made as to how a subsample is to be taken so project needs are met. This decision must be made in conjunction with the project personnel who submitted the samples for analysis. The following options are possible solutions in producing a representative subsample of a heterogeneous material.
- C Achieving a representative subsample must consider whether PSR or PSS techniques are required. If PSR or PSS techniques are used, implement the appropriate quality controls to ensure that samples are not contaminated or cross-contaminated.
- C PSR should be avoided for semivolatile organic procedures due to the potential loss of more volatile analytes. Other general considerations include contamination and cross-contamination that may result from the devices used during these techniques. If PSR is necessary, mortar and pestle is usually the best alternative for semivolatile methods. Milling is also an effective technique, but samples must be dry or dried, therefore less desirable for semivolatile methods.
- C If PSR techniques are used that require dry samples, they should be dried at room temperature to a constant weight without exposure to direct sunlight or heat.

- C If the sample is amenable to PSR (e.g., grinding or milling), refer to general guidance presented previously and process the entire sample in an appropriate device (meaning that target analytes are unaffected by the use of the particular grinding apparatus).
- C After PSR, use appropriate sieve (PSS) to check for oversized material.
- C Do not rework the oversized material. Add more original sample to the PSR equipment and repeat procedures until a sufficient amount of material is generated.
- C Following PSR/PSS techniques, mix the sample until homogeneous and subsample as outlined previously.
- C If the heterogeneity is due to foreign material or debris (and project DQOs allow), physically separate the foreign material, mix the remaining homogeneous sample, and transfer an appropriately homogeneous sample to an appropriately sized aliquot to the tared testing vessel(s).
- C Or cone and quarter the samples as outlined in Instruction E-2, repeating this procedure until the subsample obtained meets the sample size of the analytical procedure.
- C For samples that segregate into size fractions easily, perform a PSS procedure (e.g., sieving).
- C Determine the percentage of each size fraction.
- C Compose a subsample that takes an appropriate percentage of each fraction.

E.5.2.2 Aqueous liquid matrix. Samples of surface water, ground water, toxicity characteristic leaching procedure extracts, wastewaters, and leachates containing <1 percent solids are sampled using the following guidelines. Evaluate the liquid sample, looking for suspended matter, multiple phases, or any other features that may require specific measures to obtain a representative subsample. This may be restricted due to the container material (i.e., amber glass). If, upon inspection, it is discovered that the sample has more than one liquid phase, or greater than 10 percent of the sample is sediment or solid fines, consult with the project technical personnel to determine sampling needs.

E.5.2.2.1 For aqueous liquids that are to be analyzed for inorganics and total metals:

- C Allow the sample and container to equilibrate to room temperature.
- C Secure the sample lid to sample jar. Then invert, or shake the sample up and down a minimum of three times.
- C Evaluate whether the rate that the suspended matter settles allows sufficient time to acquire a representative aliquot.
- C If the suspended matter settles slowly, shake the sample repeatedly and take an aliquot immediately following procedures outlined in the following procedures.
- C If the suspended matter settles rapidly, shake the sample repeatedly and immediately transfer to a large beaker. Add a magnetic stir bar and magnetically stir the sample until uniformly mixed. While stirring continues, take an aliquot by pipet or other subsampling means.

- C Remove lid and quickly yet smoothly transfer desired aliquot into an appropriately sized graduated cylinder or volumetric flask. This choice will be dependent on the required accuracy necessary for the measurement device as specified in the applicable method. If the required sample volume is small, a volumetric pipet may be used to obtain the sample.
- C Transfer the sample from the pipet or graduated cylinder into an appropriate container used to process the subsample further.
- C If the cylinder or pipet used to subsample is to be reused for other samples, thoroughly decontaminate the transfer glassware.

E.5.2.2.2 For aqueous liquids that are to be analyzed for VOA analysis, a closed system autosampler or the following may be used:

- C Allow the VOA vials to equilibrate to room temperature.
- C Suspended particulates in volatile organic samples should be allowed to settle and are not subsampled.
- C A gastight syringe may be inserted through the septum of the vial to withdraw the sample. Or recommend the following be done when the sample size taken is greater than 5 mL.
- C Remove the plunger from an appropriately sized syringe and attach a closed syringe valve. If lower detection limits are required, use a 25-mL syringe. Open the sample bottle, and carefully pour the sample into the syringe barrel to just short of overflowing. Replace the syringe plunger and compress the sample. Open the syringe valve and vent any residual air while adjusting the sample volume to 5.0 mL or 25.0 mL. This process of taking an aliquot destroys the validity of the liquid sample for future analysis; therefore, if there is only one VOA vial, the analyst should fill a second syringe at this time to protect against possible loss of sample integrity. This second sample is maintained only until the analyst has determined that the first sample has been analyzed properly. If a second analysis is needed, it should be analyzed within 24 hours. Care must be taken to prevent air from leaking into the syringe.
- C When sample dilution is necessary, samples can be diluted before purging. This can be performed directly in the 5-mL syringe that has been filled with reagent water through the use of appropriate microliter syringes, or with volumetric glassware, as appropriate.
- C Add appropriate volumes (i.e., 10.0 : L) of surrogate standard solution, matrix spiking solution, and internal standard spiking solution through the valve bore of the syringe; then close the valve.
- C Attach the syringe-syringe valve assembly to the valve on the purging device. Open the syringe valves and inject the sample into the purging chamber. Follow appropriate procedures for purging and analysis.

E.5.2.2.3 For aqueous liquids that are to be analyzed for extractable organic analysis:

- C For samples destined for extractable organic analysis, it is recommended to utilize the entire contents of the 1-L sample container, and rinse the bottle with the appropriate solvent to avoid the loss of any compounds that may adhere to the walls of the container or cap.

- C Allow the sample and container to equilibrate to room temperature.
- C Mark the volume on the outside of the 1 L-sample bottle.

Note: If a bottle larger than 1 L is received, an aliquot should be poured into a graduated cylinder and then transferred into the extraction vessel. The appropriate organic solvent is then used to rinse the graduated cylinder. (Note this procedure runs the risk of generating an unrepresentative subsample.)

- C Make sure sample lid is attached securely and shake the sample up and down (or end over end) a minimum of three times.
- C Pour the sample smoothly into the extraction vessel.
- C Rinse the sample bottle three times with small volumes of the appropriate organic solvent and transfer these rinsates into the extraction vessel containing the sample.
- C Fill the sample bottle to the mark with tap water and pour the water into a graduated cylinder to determine the sample volume.
- C For liquid samples with suspended matter (\$1.0 percent), this subsampling procedure may induce analytical problems (i.e., the formation of an emulsion, or sediments clogging up separatory funnel). Deviations to these procedures (i.e., decanting the liquid with no mixing, no solvent rinsing of the bottle, etc.) should be identified within the case narrative.

E.5.2.3 Multiphase matrices - liquids/solids/sludges (both aqueous and nonaqueous). This section addresses samples considered multiphasic based on physical characteristics (mixture of solids and liquids). The choice of the procedure for handling multiphasic samples is highly dependent on project needs. Therefore, proper communication between project personnel and the laboratory is required in order to select the best approach to follow. If no clear guidance on project-specific needs is provided, analyst judgment must be used to decide what portions will be subsampled and the information documented within the case narrative. There are no specific procedures describing how samples with certain volume distributions or characteristics of liquid/solid are to be handled. However, the following general guidelines and three approaches are provided.

- C Nonaqueous liquids require mixing if minor particle matter is present.
- C Due to the different viscosities, densities, and coating properties, the weight of the subsample should typically be determined, rather than attempting to express the subsample in terms of volume. Anytime it is difficult to volumetrically measure a sample because it adheres to glassware walls, weight must be used.
- C If a specific and accurate weight needs to be aliquoted, a serological pipet is a good option for subsampling. Aspirate the sample, and then carefully transfer the sample into a tared vessel, controlling the addition by finger pressure on the top of the serological pipet.

E.5.2.3.1 Subsampling of samples analyzed as a single mixed phase (as received):

- C This approach will not provide information on the abundance of analytes in the individual phases.

- C The sample is mixed sufficiently to create a homogeneous sample. This is usually assessed on a visual basis. A single analysis will then be performed.
- C The manner in which the sample is mixed is highly dependent on sample consistency and how easily the phases mix. Some samples can simply be shaken, while others will require a spatula or mixing rod, or laboratory blender. If this is necessary, the device used to mix the sample must be noncontaminating, inert, and easily decontaminated. Usually a glass or Teflon-coated device is appropriate.
- C The sample is then poured, subsampled with a scoop, or transferred by some other physical means into a tared vessel and the weight of the sample is recorded. This transfer is dependent upon sample viscosity/consistency. Another consideration is not to allow the sample to resegregate into the phases when aliquoting the sample.

E.5.2.3.2 Subsampling of samples analyzed as separate phases. When the phases of a multiphasic sample are to be tested individually, the phases are separated by physical means (i.e., filtration (either pressurized or nonpressurized), centrifugation, settling, or use of a separatory funnel). The technique used is dependent on items such as laboratory capabilities, sample characteristics, and analytes of interest.

- C If an aliquot (subsample) of a sample is to be phase-separated, this aliquot must be representative of the original sample. This means that the solid and liquid ratio of the aliquot needs to be the same as the original sample.
- C To accomplish this, follow the procedures in Section E.5.2.3.1 for subsampling of samples analyzed as a single mixed phase, except that the final step is to aliquot the subsample into the device used to accomplish phase separation.
- C Items to consider when performing the phase separation include the following: device is noncontaminating, is nonabsorbent for analytes of interest, and does not cause the loss of analytes via other means.
- C Once the phases are separated, the solid and liquid ratios are determined and recorded. The two portions are transferred into either sample preparation vessels, testing vessels, or appropriate storage containers for later analysis.
- C If the liquid portion requires subsampling, follow the procedures listed in Section E.5.2.2. If the solid portion requires subsampling, follow procedures in Section E.5.2.1.
- C When phases are separated and analyzed separately, the final concentration for the total sample must be calculated mathematically. The final analyte concentration is expressed as : g/mL or : g/g.

E.5.2.3.3 If samples are to be analyzed as separated phases and only select phases are desired, then separate the phases as described in Section 3.5.2.3.2, discard those phases that are not of interest, and transfer portions of the phase(s) to be analyzed into appropriate preparation vessels following procedures described in Sections E.5.2.1 or E.5.2.2 as necessary.

E.5.3 Potential problems.

E.5.3.1 The most significant potential problem is the high probability of a subsample taken from a heterogenous waste being nonrepresentative.

E.5.3.2 Care must be exercised so that the introduction of contamination or potential for cross-contamination from equipment used to manipulate the sample is minimized. Full decontamination protocols must be performed on equipment between each use, and/or sufficient equipment must be available for individual sample usage. Recommend implementing the appropriate quality controls to ensure that samples are not contaminated or cross-contaminated.

E.5.3.3 Subsampling the lower phases of a multiphase liquid may pose special problems. A pipet or syringe needle passing through the lighter layers may pick up and transfer contaminants that can bias analytical results. The pipet tip or syringe needle should be wiped clean before transferring lower phase subsample to a preparation flask. Removal of the lighter layer(s) prior to subsampling may be required to obtain a representative aliquot.

E.5.3.4 Clay soil samples may be difficult to subsample with a coring-type device. Some hand coring samplers are equipped with clear plastic liner tubes that make extracting the subsample from the corer much easier. However, the goal is to obtain a representative sample. In these situations, professional judgment is required and a clean stainless steel spatula may be the tool of choice.

E.6 Decontamination Procedures

E.6.1 Scope and application. This section provides instruction on deciding on an appropriate decontamination scheme(s) for the project field sampling equipment to prevent or reduce cross-contamination of project samples. The applicability of each step in a decontamination protocol and the procedures used will depend upon the contaminants present onsite, the subsequent analysis to be performed, and the composition and type of sampling devices being decontaminated. The appropriateness of the decontamination protocol is vital to the eventual validity of the analytical results and decisions made based upon those results. All sampling equipment that contacts potentially contaminated media must be cleaned before the subsequent use of that device. Devices may include bailers, pumps, shovels, scoops, split spoons, tube samplers, augers, etc. Another approach to minimizing the potential for cross-contamination may be to dedicate or use disposable sampling equipment.

E.6.2 Decontamination procedures. Refer to Table E-3 for various stepwise decontamination protocols for sampling equipment that comes in direct contact with the sample. Each protocol begins with the detergent wash, followed by a series of chemical and water rinses, and concludes with an air-drying step. Additional guidance and protocols for the staging or setup of decontamination procedures may be found in National Institute for Occupational Safety and Health (1985) and ASTM Standards D 5088 and D 5608. To

Table E-3
Recommended Decontamination Procedures¹

	Detergent Wash	Tap Water	Inorganic Desorbing Agents	Tap Water	Organic Desorbing Agents	Deionized Water	Air Dry
VOA							
Low MW CMPDS ²	T	T			Methanol	T	T
BNA/PEST/PCBS							
High MW CMPDS ²	T	T			Hexane	T	T
Organic Bases ³	T	T	(1%)	T	Isopropyl alcohol	T	T
Organic Acids ⁴	T	T			Isopropyl alcohol	T	T
Trace metals	T	T	(10%)	T		T	T
Salts	T	T				T	T
Acidic CMPDS	T	T				T	T
Basic CMPDS (caustic)	T	T	(1%)	T		T	T

¹ Solvent rinses vary in polarity which leads to varying solubilizing properties. The selection of appropriate solvent rinses should first consider if a known or suspected contaminant requires removal from sampling equipment. Optimum solvents for contaminants are noted. Secondly, identify whether the subsequent analytical protocol would be impacted by the proposed solvent or an impurity thereof (e.g., residual acetone present in isopropyl alcohol would be measured with certain volatile organics analysis).

² MW CMPDS = molecular weight compounds.

³ Organic bases include amines, hydrazines.

⁴ Organic acids include phenols, thiols, nitro and sulfonic compounds.

evaluate and document the effectiveness of the decontamination protocol, recommend the acquisition of final rinsates or wipe samples after equipment decontamination procedures are completed. Refer to Instruction G-2, Appendix G, and Instruction C-7, Appendix C, for information on the acquisition of rinsates and wipe samples, respectively.

E.6.2.1 Reagents. Reagents necessary will vary based on the protocol chosen. The following outlines general guidance for the typical reagents used to support decontamination procedures. The detergent wash is a nonphosphate detergent solution used with brushing or circulating techniques to remove gross contamination, and/or as a mild neutralizing agent. Tap water from a water system of known chemical composition is considered a control rinse water. Inorganic desorbing agents are dilute nitric or hydrochloric acid rinses. Due to their corrosive nature, the inorganic desorbing rinses may be omitted from decontamination procedures associated with metallic or stainless steel sampling devices at the discretion of project personnel. Solvent rinses (i.e., isopropyl alcohol, methanol, or hexane) are used as an organic desorbing agent. The solvent chosen must be effective in removing the organic contamination present, but must also be compatible with the subsequent analyses performed. Care should be taken to use an appropriate grade of solvent to minimize the potential introduction of impurities present in the organic desorbing rinse that may interfere or contribute to the subsequent analysis. For this reason, recommend that all solvent rinses used be appropriate grade, such as pesticide or purge-and-trap grade quality. Finally, the deionized water is organic-free reagent water.

E.6.2.2 Procedure clarifications/exceptions.

E.6.2.2.1 Table E-3 refers to the general recommended procedures used to decontaminate sampling equipment. Depending upon site contaminants, degree of contamination, analytical protocols, and composition and type of sampling equipment used, the project chemist may determine to modify or eliminate various steps of the decontamination procedures outlined in Table E-3.

E.6.2.2.2 As noted previously, the detergent wash is used in conjunction with scrubbing for gross contamination removal, followed by the appropriate rinses. For cleaning of pumping equipment or devices with inaccessible internal mechanisms, suggest circulating/flushing the system with the applicable solutions in the following order. For sampling probes used for soil gas sampling procedures, decontaminate by removing visible soil and drawing ambient air through them. Alternatively, volatiles may be baked off the soil gas probe using a portable heater. Water and solvent rinses should not be used on soil gas sampling probes. Solvent rinses for water pumping equipment should be limited to a 10 percent dilution (volume/volume) of acetone or isopropyl alcohol in water. Tubing used with peristaltic pumps may be dedicated or may be flushed with hexane, followed by a distilled water rinse depending on contaminants noted onsite. All sampling equipment should be allowed to dry prior to the next use. For this reason it is important to have sufficient sampling devices onsite so that they may be alternated. This practice will allow a thorough drying of equipment without increasing sampling downtime. If sampling equipment is not used immediately, wrap within an inert material (i.e., aluminum foil) to avoid contact with potentially contaminating materials. Equipment that does not directly contact the sample, such as large drilling equipment, drill-rig components, power augers, etc. should be cleaned with a portable power washer or a steam-cleaning machine. Finally, depending upon the project, it may be appropriate to contain spent decontamination fluids and arrange for eventual disposal as investigation-derived wastes. These containers may also be used for the eventual disposition of the materials, and therefore must comply with any potentially applicable DOT regulations.

E.6.3 Sample contaminant sources and other potential problems.

E.6.3.1 Carryover and leaching. Contaminant carryover between samples and/or from leaching of the sampling device is very complex and requires special attention. Decisions concerning the appropriateness of the material composition of the device must account for these carryover or leaching potentials, and whether these contaminants are of concern on the project. Materials potentially encountered on projects and their associated common contaminants are listed in Table E-4.

E.6.3.2 Adsorption. Contaminant adsorption is another problem that must be considered when deciding on an applicable sampling device or the appropriate composition material. This phenomenon is more critical when sampling an aqueous or gaseous media, due to the capability of lower levels of contaminant detection and the fact that the fluid matrix is more susceptible to potential contaminant transfer. PVC and other plastics are known to sorb organics and to leach plasticizers and phthalate esters. Polypropylene and other thermoplastics have been shown to sorb organics and environmental mercury efficiently and should, therefore, be avoided in sampling devices, especially tubing. For these reasons, PTFE is commonly chosen over the PVC and plastics when working with organic or mercury contaminants. In addition, some pesticides and halogenated compounds preferentially adsorb to glass surfaces. For this reason, it is recommended that when aqueous samples are taken, the sample container NOT be rinsed prior to sample collection, and the same container be rinsed with the extraction solvent after the sample has been quantitatively transferred to an extraction apparatus. Inorganics (metals) adsorption to containers is dependent upon the specific metal element, the concentration, pH, contact time, complexing agents present, and container composition. This is believed to be nominal, and proper preservation of samples should prevent this. In selecting appropriate tubing to be used for aqueous sample acquisitions, it is important to decide applicable material composition and diameter based upon the contaminant and the purpose of the data. Adsorption is less likely to occur when there is a increase in tubing diameter.

Table E-4
Materials Potentially Encountered on Projects

Material	Commonly Related Contaminants
Glass	Silicon Boron
Rigid PVC (threaded joints)	Chloroform Vinyl chloride
Rigid PVC (cemented joints)	Methyl ethyl ketone Toluene Acetone Methylene chloride Benzene Tetrahydrofuran Ethyl acetate Cyclohexanone Vinyl chloride
PVC plastic tubing	Phthalate esters Vinyl chloride Low level (zinc, iron, antimony, and copper)
Soldered pipes	Lead Tin
Stainless steel	Chromium Iron Nickel Molybdenum
Brass	Copper Zinc Tin